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CANON KK *J6 2096-566-A
24.10.85-JP-236390 *(06.05.87)* C08k-07 C08l-101
Moulded resin prod. for e.g. camera case - contains thermoplastic resin e.g. styrene and lustrous particles e.g aluminium
C87-068853

A(8-E1, 11-A1A, 11-B1)

Moulded resin prod. comprises 100 vol.pts. of thermoplastic resin and lustrous particle (with 10-300 micron average dia., and average shape ratio of 1/8-1). The deg. of reflection of the prod. is higher than before moulding by more than 15%.

Content of lustrous particle is 0.05-5.0 vol.pts. (pref. 0.3-3.0) per 100 vol.pts. of resin. Pref. increase in deg. of reflection is 25-80%. Lustrous particle is e.g. Al, Sn, Cu, Fe, brass, s/s, mica, shell, polymer with double refraction property, etc. Al particle gives silivery, glazed appearance, and brass particle gives solid, golden appearance. Thermoplastic resin is e.g. acrylic resin, polystyrene, PVC, etc. Colouring material can be added in amt. 0.1-12.0 vol.% per 100 pts. resin.

USE/ADVANTAGE - Prod. is used as interior/exterior material and containers for camera, VTR, OA equipment, electric razor, and cosmetics. Prod. has no weld-mark and good appearance. (5pp Dwg.No.0/7)

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(54) Title of the invention: Resin moulded articles

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Specification

1. Title of the Invention

Resin moulded articles

2. Scope of Claim

Resin moulded articles which are characterized in that they contain, per 100 parts by volume of thermoplastic resin, from 0.05 to 5.0 parts by volume of lustrous particles of mean equivalent diameter 10 to 300 μm and mean shape factor 1/8 to 1, and the reflectance is raised by at least 15% compared to the state not containing such lustrous particles.

3. Detailed Description of the Invention

[Industrial Field of Application]

The present invention relates to resin moulded articles which are used for cameras, VTRs, OA equipment, electric razors, interior and exterior decorative materials for cosmetic products, containers and the like.

[Prior-Art]

There are many known examples of moulded articles produced by mixing together and then melting and moulding a thermoplastic resin and a filler material such as metal particles for conferring a lustrous external appearance. Depending on the shape of the lustre-conferring particles, these moulded articles fall into two categories. The first, as disclosed in JP-A-58-37045, comprises moulded articles where the entire face is given a uniform metal-like appearance, that is

to say a metallic tone, by filling the resin with fine or superfine metal powder particles. When such moulded articles are produced by injection moulding, as can be seen in the flow sections of the molten resin within the mould illustrated in Figure 2 and Figure 3, a layer **22** which does not contain metal particles is formed at the front of the flow during the flow process (Figure 2), so that a weld mark **23** (Figure 3) comprising resin alone is formed at the weld between the two melt flows. Since this weld mark does not contain metal particles, light is absorbed and it looks black, so the appearance is markedly impaired. Consequently, such a moulded article cannot be used as a camera outer cover or other such high grade moulded article.

The second category comprises the use of a metal flake powder having a mean equivalent diameter of at least 30 μm and a mean shape factor of 1/10 or less. With such moulded articles, at the time of the kneading and moulding of the resin and metal flake powder, the flake powder is subjected to shear and breaks up. If there is no such break-up, the weld mark in the moulded article becomes inconspicuous but if break-up does occur then this results in a conspicuous weld mark just as is seen in the first category described above.

Now, Figure 4 and Figure 5 show the particle size distributions before and after the kneading and moulding of an aluminium flake powder of mean equivalent diameter 50 μm and mean shape factor 1/10 or less. In this case, the weld mark becomes conspicuous and use as a high grade moulded article of complex shape is difficult.

Moreover, besides weld marks, other causes of a defective appearance in moulded articles include uneven gloss, sink marks, silver streaks and the like. For example, in a moulded article of basic wall thickness 2 mm, if there is a local thin-wall region present of thickness 1.5 mm as illustrated in Figure 6, with for example a polycarbonate resin moulded article a 5-10 μm difference in level arises in exterior appearance region **61** and this is seen as an uneven gloss. Again, if a local thick-wall region of thickness 3.0 mm is present in a moulded article of basic wall thickness 2 mm as illustrated in Figure 7, a 5-10 μm difference in level arises in the arrowed exterior appearance region **71** and this is conspicuous as a sink mark[i].

In order to ensure that such uneven gloss or sink marks are not conspicuous, attempts have been made hitherto to carry out high mould temperature moulding but, when high mould temperature moulding is conducted, the moulding time is extended and productivity lowered. Moreover, while the uneven gloss and sink marks are somewhat less conspicuous, it is not possible to eliminate them completely.

Hence, as a means for eliminating such defects in appearance, painting or other such secondary processing has been necessary or the product design has been adjusted so that such defects in appearance are not manifested, but the restrictions in terms of product design then become very considerable.

Again, another problem in the case of obtaining the final moulded article merely by injection moulding is that the surface hardness of the resin itself is low,

and scratches[ii] are readily introduced. Once a scratch has been introduced, this has a considerable influence on the appearance and often a high grade appearance is not achieved.

[Objective and Features of the Invention]

A first objective of the present invention lies in offering resin moulded articles which are free of defects in appearance caused by the weld marks seen in conventional resin moulded articles filled with lustre-conferring particles.

A second objective of the present invention lies in offering resin moulded articles which, as well as being free of such weld marks, do not have any conspicuous defects in appearance due to uneven gloss, sink marks and silver streaks, etc, and furthermore, where the appearance is not markedly impaired even when scratches are introduced.

A third objective lies in providing resin moulded articles which, as well as being free of such defects in appearance, also have an outstanding appearance, namely a glittering appearance like stars scattered in the clear night sky (below this is referred to as a star[iii]-like appearance), enabling such a resin moulded article to be used for complex-shaped high-grade moulded articles like camera outer covers and VTR covers, etc.

A fourth objective lies in providing resin moulded articles which enable the design restrictions imposed at the time of product design of the moulded articles in order to overcome defects in appearance to be lifted.

The aforesaid objectives are realized by means of the resin moulded articles of the present invention which are characterized in that they contain, per 100 parts by volume of thermoplastic resin, from 0.05 to 5.0 parts by volume of lustrous particles of mean equivalent diameter 10 to 300 μm and mean shape factor 1/8 to 1, and the reflectance is raised by at least 15% compared to the state not containing such lustrous particles.

[Detailed Explanation of the Invention and Examples thereof]

The aforesaid lustrous particles which are used in the present invention are particles with a mean equivalent diameter of 10 to 300 μm and having a mean shape factor of 1/8 to 1.

Taking the arithmetic mean of the maximum diameter and the minimum diameter of a lustrous particle as its equivalent diameter, the mean equivalent diameter refers to the value obtained by averaging the equivalent diameters for a group of test particles. The measurement of the equivalent diameter can be carried out using a Luzex particle distribution measurement device (commercial product name; produced by Nippon Regulator K.K. [Nireco]), with the moulded article placed on a glass plate either in the as-moulded state or after dissolving in solvent.

Furthermore, the mean shape factor refers to the arithmetic mean of the ratios of the maximum to the minimum diameters of the particles, that is to say (minimum diameter)/(maximum diameter). In calculating

the mean shape factor, there can again be used the Luzex particle distribution measurement device.

Assuming the lustrous particles to be spherical, in a system in which the spheres are distributed in such a way that the distance between their centres is the same, the average space between the lustrous particles is expressed by formula (1).

$$D = R \left(\sqrt[3]{\frac{\pi}{3\sqrt{2}\,V}} - 1 \right) \qquad (1)$$

where

D: average space between lustrous particles

R: mean equivalent diameter of the lustrous particles

V: volume ratio of all the lustrous particles in terms of the total volume of thermoplastic resin and lustrous particles

D is an index of how conspicuous the weld mark is, and the greater the value of D the less conspicuous is the weld mark. That is to say, normally the width of a metallic mould weld mark is no more than 30 μm, so if D is greater than 35 μm then the weld mark will tend not to be conspicuous.

The appropriate mean equivalent diameter of the particles such that D is at least 35 μm and, furthermore, such that a star-like appearance is shown is 10-300 μm. If the mean equivalent diameter is less than 10 μm, then as well as weld marks and other such defects in appearance being conspicuous, it becomes difficult to distinguish the individual particles by

eye, and there is merely a change in colour tone. Furthermore, there is little effect in making scratches inconspicuous.

If the mean equivalent diameter is more than 300 μm, the lustrous particles are just seen as 'foreign matter', the balance in terms of appearance is impaired and a good external appearance is not obtained. The particularly preferred range for the mean equivalent diameter is 20-100 μm.

Again, the reason for the mean shape factor of the lustrous particles used in the present invention being in the range 1/8 to 1 is that, if this factor is less than 1/8, breakdown of the lustrous particles will tend to occur at the time of kneading/moulding and the weld marks will tend to become more conspicuous. The range 1/3 to 1 is particularly preferred as the mean shape factor.

Furthermore, it is necessary for the content of the lustrous particles to be in the range 0.05 to 5.0 parts by volume per 100 parts by volume of the thermoplastic resin, with the range 0.3 to 3.0 parts per volume being particularly preferred. If the amount of lustrous particles is less than 0.05 part by volume, then the particles are too sparsely scattered and there is hardly any effect in making the defects in appearance and scratches inconspicuous. If the amount is more than 5.0 parts by volume, then the colour tone of the particles will determine the colour tone of the moulded article and no star-like appearance is produced.

In addition, in the resin moulded articles of the present invention, another essential condition for eliminating the defects in appearance and producing an excellent external appearance is that the reflectance of the resin moulded article be raised at least 15% compared to the state not containing lustrous particles.

Here, reflectance refers to the reflectance measured using a Photonics Sensor (commercial product name of the Photonics Co.), by a method in which the moulded article is placed on a support stand, then light directed thereat with a probe perpendicularly arranged, and the reflected light measured.

Where the percentage rise in the reflectance is less than 15%, this is insufficient to render the defects in appearance and scratches inconspicuous. Moreover, there is imperfect manifestation of the star-like appearance. The percentage rise in reflectance is more preferably 25-80%.

Any material can be used for the lustrous particles employed in the present invention, providing that they are particles possessing lustre at the surface. For example, it is possible to use lustrous particles at least the surface layer region of which comprises a metal like aluminium, tin, copper or iron, alloys based on such metals such as brass or stainless steel, and mica, various types of shell, inorganic or organic polymer crystals of the kind which give rise to birefringence, phosphors or the like.

When, for example, aluminium particles are used, there is obtained a glittering silver appearance, while when

brass particles are used there is obtained a soft golden appearance. Again, it is possible to form a variety of appearances by changing the surface lustre of the metal particles.

The resin employed in the present invention is for example a thermoplastic resin such as an acrylic resin, polystyrene resin, polypropylene resin or other such polyolefin resin, vinyl chloride resin, methyl pentene resin, polycarbonate resin, copolyester, copolyamide, ABS or the like, or mixtures of these, and it may also be coloured. Furthermore, it is also possible to form a still greater variety of appearances by mixing a colouring agent into the resin moulded article of the present invention, for example 0.1 to 12.0 parts by volume thereof per 100 parts by volume of the resin.

Again, it is also possible to add the various stabilizers, mould release agents, antistatic agents, flame retardants and the like which may be incorporated into thermoplastic resins, providing the amount lies within a range such that the effects of the invention are not impaired.

In the case where the resin moulded articles of the present invention are produced by injection moulding or injection compression moulding, the effects of the invention are particularly manifested but there may also be used other types of molten moulding methods such as extrusion.

Silver streaks, which are another type of defect in appearance, have long been said to readily occur when moulding to provide a metallic appearance, but by making

the drying time at least 2 hours and ensuring that the mould temperature does not drop, there is no occurrence of silver streaks in the case of the star-like appearance. Furthermore, in the case of a metallic tone, a pinpoint moulding gate increases the occurrence of silver streaks but, with the star-like appearance of the present invention, silver streaks do not occur even with a pinpoint gate.

In terms of uniformly dispersing the lustrous particles in the moulded article, the thermoplastic resin and lustrous particles are preferably used in the form of a composition such as, for example, pellets obtained by prior melting and mixing of the resin.

Below, the present invention is explained in still more specific terms by means of examples.

Example 1

Resin moulded article **1** shown in Figure 1 [(a) being a plan view thereof, and (b) a sectional view through A-A'] was produced by injection moulding. Moulded article **1** was a flat plate of length 100 mm and width 80 mm, and its basic thickness was 1.6 mm. It was provided with thick regions **2** and **3** of thickness 2.6 mm and 2.0 mm respectively and thin regions **4** and **5** of thickness 1.2 mm and 0.8 mm respectively. The moulded article comprised coloured ABS resin containing 1.0 part by volume of aluminium particles of mean equivalent diameter 52 μm and mean shape factor 1/3.7, per 100 parts by volume of the resin, and was moulded under the following *{sic}*[iv] conditions.

The reflectance of the moulded article obtained was raised 56.7% compared to the state not containing aluminium particles. There were no defects in appearance such as weld marks, uneven gloss or sink marks, etc, nor did scratching readily occur. In terms of external appearance, a brightly glittering high grade appearance was obtained which was fully suitable for use as a camera cover.

Examples 2 and 3

Moulded articles were obtained in the same way as in Example 1 except that the mean equivalent diameter of the aluminium particles used was changed to 92 μm or to 210 μm. In the same way as in Example 1, the moulded articles obtained showed no defects in terms of appearance and they had a high grade appearance.

Examples 4 and 5

Moulded articles were obtained in the same way as in Example 1 except that the content of the aluminium particles was changed to 0.1 part by volume or to 2.5 parts by volume per 100 parts by volume of the ABS resin. In the same way as in Example 1, the moulded articles obtained had no defects in terms of appearance and they had a high grade appearance.

Examples 6 and 7

Moulded articles were obtained in the same way as in Example 1 except that the mean shape factor of the aluminium particles was changed to 1/7.2 or to 1/1.6. In the same way as in Example 1, the moulded articles

obtained had no defects in terms of appearance and they had a high grade appearance.

Examples 8 and 9

The moulded article of Example 1 was produced using 100 parts by volume of coloured polycarbonate resin and 1.5 parts by volume of either of two different types of aluminium particles having a mean shape factor of 1/1.6 (mean equivalent diameter 42 μm) or a mean shape factor of 1/7.2 (mean equivalent diameter 50 μm). The percentage rise in reflectance of the moulded articles produced was 28% in the 1/16 shape factor case and 97% in the 1/7.2 shape factor case. The moulded articles obtained had no defects in terms of appearance and they had a high grade appearance.

Comparative Example 1

Using a 0.03 part by volume content of aluminium particles of mean equivalent diameter 8 μm and mean shape factor 1/1.4, per 100 parts by volume of coloured ABS resin, moulding was carried out under the same moulding conditions as in Example 1.

The reflectance of the moulded article obtained was raised 7% compared to the state containing no aluminium particles.

However, welds, uneven gloss, sink marks and the like were conspicuous and the scratches were essentially no different from ordinary ABS. The moulded article could not be used as a moulding of high grade appearance.

Comparative Example 2

Moulding was carried out in the same way as in Example 1 with ABS resin which did not contain aluminium particles. Uneven gloss, sink marks and the like were very conspicuous, such that the moulded article could not be used as a manufactured product. (Surface hardness 3B)

[Effects of the Invention]

The resin moulded articles of the present invention are free of weld marks and there are no defects in appearance due to uneven gloss, sink marks, silver streaks and the like and, furthermore, there is no marked impairment of appearance due to scratches. Moreover, there is provided a star-like external appearance which can be used for high grade moulded articles such as camera outer covers, typewriter covers and the outer covers of OA equipment, etc, and it is possible to broaden the design limits of the appearance of plastics. This has not been achievable hitherto. In particular, in the case where thermoplastic resins which have been coloured by colouring agents are employed, the effects of the invention are remarkable and the invention may also be applied to articles of complex shape.

Moreover, design limitations aimed at mitigating defects in appearance are removed and design freedom enhanced. Productivity is also raised.

4. Brief Explanation of the Drawings

Figure 1(a) is a plan view of a resin moulded article of the present invention produced in the examples, and Figure 1(b) is a sectional view along A-A' in Figure 1(a).

Figure 2 is a sectional view of the flow of a conventional metal-filled resin; Figure 3 is a sectional view after moulding of the metal-filled resin; Figure 4 and Figure 5 are graphs showing the particle size distribution (frequency distribution) before and after moulding in the case where lustrous particles of mean shape factor 1/10 or less are used.

Figure 6 and Figures 7 are respectively sectional views for indicating locations of the occurrence of uneven gloss and sink marks, etc, in a resin moulded article.

1 ... resin moulded article, 2,3 ... thick regions, 4,5 ... thin regions, 21 ... metal powder, 22 ... layer of resin alone, 23 weld mark

Agent Patent Attorney J. Yamashita

Figure 1

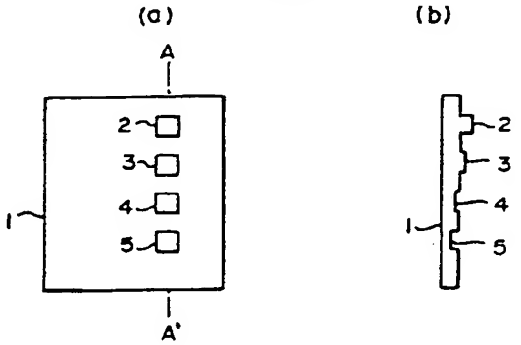


Figure 2

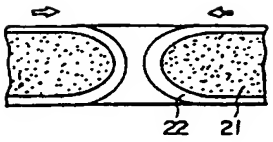


Figure 3

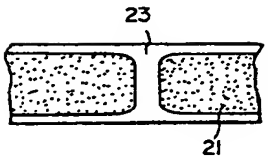


Figure 4

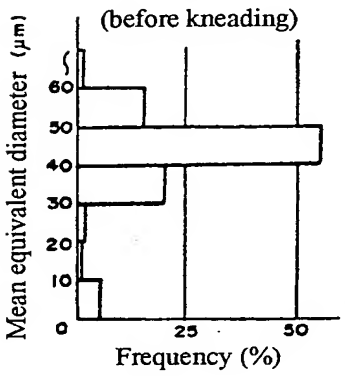


Figure 5

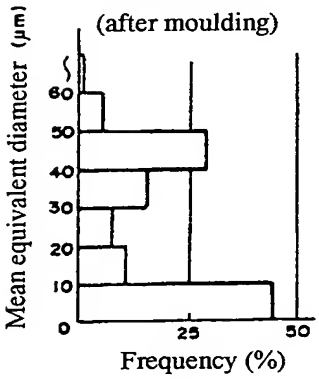


Figure 6

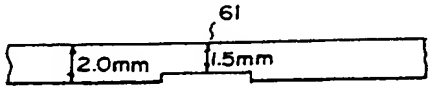
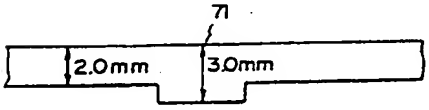


Figure 7



Translator's Notes

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[i] The usual translation of the Japanese term 'hiké' is sink mark (or shrink mark) but here the effect would seem to be the exact opposite of sinking (or shrinking).

[ii] The Japanese term used may have a broader meaning than just a 'scratch'. In some dictionaries it is broadly translated as a 'mark'. However, 'scratch' is a common meaning of the term used.

[iii] The Japanese term 'ginga' translates as "milky way" or "a galaxy". The meaning here would seem to suggest numerous glittering star-like points of light.

[iv] No conditions are given in the original text.